

CLAIMS

1. Mixture of particles comprising a non-conducting or semi-conducting nucleus, the nuclei of said particles being at least partially covered with a hybrid conductor coating and said particles being at least partially connected through hybrid conducting chains which provide a network of electrical conductivity.
2. Mixture according to claim 1, in which the particles comprise a non-conducting or semi-conducting nucleus and a coating, at least partially made of a hybrid conductor material, and in which said particles are at least partially interconnected through hybrid conducting chains.
3. Mixture according to claim 1 or 2, in which the coating comprises a mixture of at least two different conducting materials and in particle form, some particles of the coating of a first nucleus being interconnected with particles of the coating of a second nucleus located in the mixture of particles proximate said first nucleus.
4. Mixture of particles according to claim 2 or 3, in which the coating comprises:
 - a first conducting material at least partially, preferably by between 50 and 90 %, and more preferably by at least 80 %, covering the surface of said nuclei; and

- a second conducting material in which preferably from 10 to 50 % (more preferably about 20 %) of the particles are connected together to constitute an electrical conductivity network.
5. Mixture according to any one of claims 1 to 4, in which the nuclei comprise at least one phosphate, one nitride, one oxide or a mixture of two or more of them.
 6. Mixture according to claim 5, in which the nucleus of said particles, in major portion, and preferably for at least 70 % by weight, consists of at least one metal oxide.
 7. Mixture according to claim 6, in which the metal oxide, for more than 65 % by weight, consists of a lithium oxide.
 8. Mixture according to claim 7, in which the lithium oxide is carbon coated.
 9. Mixture according to any one of claims 6 to 9, in which the nucleus consists of a lithium oxide of spinel structure.
 10. Mixture of particles according to any one of claims 6 to 9, in which the lithium oxide is selected from the group consisting of oxides of the formula:
 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$;

- $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$, in which α is higher than 0 and lower than or equal to 0.33, Z represents a source of at least one metal; and
 - $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ in which β is higher than 0 and/or lower than or equal to 0.5, Z represents a source of at least one metal.
11. Mixture according to claim 10, in which at least 65 % of the nucleus of the particles consists of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ or a mixture thereof, α and β having the values defined in claim 10.
 12. Mixture according to claim 9, in which the nucleus of particles consists of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$, $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ or a mixture thereof, α and β having the values defined in claim 10.
 13. Mixture according to claim 1, in which the nucleus of said particles is semi-conducting and consists of a material selected from the group consisting of Si, doped Si, or Ge, Ge and InSb.
 14. Mixture according to claim 1, in which the nucleus of said particles is non conducting and consists of a material selected from the group consisting of glasses, mica and SiO_2 .
 15. Mixture according to claim 1, in which the particles have a D_{50} of 7 micrometers.
 16. Mixture according to any one of claims 9 to 11, in which Z represents a particle of a metal selected from the group consisting of Mg, Nb, Al, Zr, Ni and Co.

17. Mixture according to any one of claims 10 to 16, in which the metal oxide has the formula $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li_2TiCO_3 , LiCoO_2 , LiNiO_2 or LiMn_2O_4 .
18. Mixture according to any one of claims 1 to 17 containing from 1 to 6 % by weight of carbon in said mixture.
19. Mixture according to claim 18 containing about 2 % by weight of carbon in said mixture.
20. Mixture according to any one of claims 1 to 19, in which the coating consists of a hybrid mixture of carbon, and/or a carbon-metal hybrid mixture.
21. Mixture according to claim 20, in which the metal is selected from the group consisting of silver, aluminum and mixtures thereof.
22. Mixture according to claim 20, in which the hybrid carbon mixture comprises at least two different conducting forms of carbon, hereinafter designated Carbon 1 and Carbon 2.
23. Mixture according to claim 22, in which Carbon 1 is a low crystallinity carbon.
24. Mixture according to claim 23, in which the crystallinity of the particles of Carbon 1, measured by X-ray diffraction and/or by Raman spectroscopy, is characterized by a d_{002} higher than 3.36 Angströms.

25. Mixture according to any one of claims 22 to 24, in which Carbon 2 is a graphite and/or a high crystallinity carbon.
26. Mixture according to claim 25, in which the crystallinity of the particles of Carbon 2, measured by X-ray diffraction is characterized by a d_{002} lower than 3.36 Angströms.
27. Mixture according to claim 26, in which Carbon 2 is a natural graphite, a synthetic graphite or an exfoliated graphite.
28. Mixture according to any one of claims 22 to 27, in which Carbon 1 has a specific surface area, measured according to the BET method, that is higher than or equal to $50 \text{ m}^2/\text{g}$.
29. Mixture according to claim 28, in which the particles of Carbon 1 that are used have an average size that varies from 10 to 999 nanometers.
30. Mixture according to any one of claims 22 to 29, in which the particles of Carbon 2 have a specific surface area measured according to the BET method, that is lower than or equal to $50 \text{ m}^2/\text{g}$.
31. Mixture according to any one of claims 22 to 30, in which the particles of carbon 2 that are used, have a size that varies from 2 to 10 micrometers.

32. Mixture according to any one of claims 22 to 31, in which Carbon 2 consists of at least one graphite selected from the group consisting of synthetic graphite, natural graphite, exfoliated graphite and mixtures of two or more of these graphite.
33. Mixture according to any one of claims 22 to 32, in which the weight percentage of Carbon 1 represents from 1 to 10% of the total weight of the coating composed of Carbon 1 and Carbon 2.
34. Mixture according to any one of claims 22 to 33, in which the quantity of Carbon 1 is substantially identical to the quantity of Carbon 2.
35. Mixture according to any one of claims 1 to 34, in which the average diameter of the nucleus of said particles varies from 50 nanometers to 30 micrometers.
36. Mixture according to claim 35, characterized in that the average diameter of said nucleus is of the order of 2 micrometers.
37. Mixture according to any one of claims 1 to 36, in which the average size of said particles, measured according to the electronic scanning microscope method, is between 4 and 30 micrometers.
38. Mixture according to any one of claims 1 to 37, having at least one of the following properties: a very good local conductivity, a very good network conductivity, a low resistivity, a very good capacity under elevated current and a good density of energy.

39. Mixture according to claim 36, having a local conductivity, measured according to the four point method, that is higher than 10^{-6} (Ohm-m) and preferably higher than or equal to 10^{-5} (Ohm-m).
40. Mixture of particles according to claim 38 or 39 having a network conductivity, measured according to the four point method, that is between 2.6×10^{-3} and 6.2×10^{-3} , and preferably lower than 6.0×10^{-3} (Ohm-m).
41. Process for preparing a mixture of particles such as defined in any one of claims 1 to 40, comprising at least one of the following steps:
 - a) preparation of a mixture of at least one non-conducting or semi-conducting material with a conducting material, and the addition of a second conducting material to the mixture obtained;
 - b) preparation of a mixture of at least one non-conducting or semi-conducting material with at least two conducting materials; and
 - c) preparation of a mixture of conducting materials and mixing thereof with at least one non-conducting or semi-conducting material.
42. Process for preparing a mixture of particles according to claim 41, in which mixing of materials is carried out by mechanical crushing of the type HEBM, Jar milling, Vapor jet milling and preferably by HEBM.
43. Process for preparing a mixture of particles according to claim 41 or 42, carried out at a temperature lower than 300 degrees Celsius,

preferably at a temperature between 20 and 40° Celsius, more preferably at room temperature.

44. Process for preparing a mixture of particles according to any one of claims 41 to 43, in which the nuclei of said particles are based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the coating is based on a mixture of carbon, mixing of carbon being carried out chemically, before the step of synthesizing particles of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
45. Process according to any one of claims 41 to 44, in which at least one of the conductor materials (Carbon 1) is obtained by thermal treatment of a polymer type precursor.
46. Process according to claim 45, in which the polymer is selected from the group consisting of natural polymers, modified natural polymers as well as mixtures thereof.
47. Process according to claim 46, in which the polymer is selected from the group consisting of sugars, chemically modified sugars, starches, chemically modified starches, gelatinized starches, chemically modified starches, chemically modified and gelatinized starches, cellulose, chemically modified cellulose and mixtures thereof.
48. Process according to claim 47, in which the polymer is a cellulose acetate.

49. Process according to any one of claims 44 to 48, in which mixing of carbon is carried out by physical admixing, after $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesis.
50. Cathode for electrochemical generator comprising a mixture of particles such as those defined in any one of claims 1 to 40 and/or particles capable of being obtained by a process according to any one of claims 41 to 49.
51. Anode for electrochemical generator comprising particles such as those defined in any one of claims 1 to 40 and/or particles capable of being obtained by a process according to any one of claims 41 to 49.
52. Electrochemical generator of the lithium type including at least one metallic lithium anode and at least one cathode such as those defined in claim 50, preferably an anode of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ type.
53. Electrochemical generator according to claim 52, preferably of the rechargeable and/or recyclable type.
54. Electrochemical generator according to claim 52 or 53 of the lithium ion type comprising at least one electrolyte, at least one anode as defined in claim 50, preferably an anode of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ type and at least one cathode of the LiFePO_4 , LiCoO_2 , LiMn_2O_4 and/or LiNiO_2 type.

55. Electrochemical generator according to any one of claims 52 to 54, in which at least one anode and/or at least one cathode are provided with an aluminum current collector that is full or of the Exmet type (expanded metal).
56. Electrochemical generator according to any one of claims 52 to 55 requiring no previous preparation of the battery.
57. Generator according to any one of claims 52 to 57, in which the electrolyte is a dry polymer, a gel, a liquid or a ceramic.
58. Hybrid type supercapacity comprising at least one electrolyte, at least one anode, such as defined in claim 51, preferably of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_{(4-\alpha)}\text{Z}_\alpha\text{Ti}_5\text{O}_{12}$ and/or $\text{Li}_4\text{Z}_\beta\text{Ti}_{(5-\beta)}\text{O}_{12}$ type and at least one cathode of the graphite or large surface area carbon type, requiring no previous preparation of the supercapacitor.
59. Supercapacity according to claim 58, in which at least one anode and/or at least one cathode are provided with an aluminum current collector that is full or of the Exmet type (expanded metal).
60. Supercapacity according to claim 59, in which the electrolyte is a dry polymer, a gel, a liquid or a ceramic.
61. Electrochemical system according to any one of claims 52 to 60, characterized in that the electrode is prepared without any addition of additional carbon.